(Revised)

# TRANSITION METAL DOPED NANOFERRITES: STUDY OF STRUCTURAL AND MAGNETIC PROPERTIES

**SYNOPSIS**

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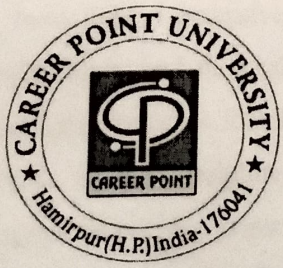
***Submitted by***

**Anil Kumar**
**Enrollment No.: H240598**

***Under the supervision of***

**Co-Supervisor**
**(Dr. Prashant Thakur,**
**Assistant Professor (Physics))**

**Supervisor**
**(Prof. (Dr.) Yogesh Kumar Walia)**




**DEPARTMENT OF CHEMISTRY**
**SCHOOL OF BASIC AND APPLIED SCIENCES**
**CAREER POINT UNIVERSITY HAMIRPUR**
**TIKKER (KHARWARIAN), BHORANJ**
**HAMIRPUR (HP)-176041, INDIA**

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## Introduction:

Nanotechnology is the synthesis and understanding of materials of size 1 nm to 100 nm. The physical as well as chemical characteristics of the nano-materials are dependent on the size, shape and morphology. So, the researchers are tending to develop easy and fruitful process for preparing nano-materials with managed shape, size, composition and morphology for improving their characteristics. A salient point about the nano-scale is that as we reduce the particle size in nano-region, the surface area becomes huge. As the size of the particles is reduced to nano-level, various properties such as electrical, magnetic, structural, mechanical etc are largely changed. Nano ferrites have very unusual properties and are very different from their bulk form. As we decrease the size, surface to volume ratio increase and properties are greatly changed. Substitution in ferrites also changes their crystalline, electrical and magnetic properties due to variation in atomic size, electronic structure, magnetic spins and their lattice site preference (Kumar et al., 2013; Khot et al., 2013). The magnetic nanoparticles which are synthesized chemically have drawn much attention due to the unique magnetic properties due to their Nano size and uniform particle size distribution. The magnetic nanoparticles produced chemically are used in high density recordings (Hylton et al., 1994; Fujiwara et al., 1985), biomedicine (Wu et al., 2011; Sun et al., 2008) and catalyst (Rezlescu et al., 2014). Spinel ferrites are a family of magnetic compounds that have attracted attention due to their distinct crystal arrangement and excellent magnetic characteristics. As a result of their outstanding magnetic characters, high electrical resistivity and low eddy current losses, these materials have ground extensive use in a variety of industries, including electronics, telecommunications and medical equipment (Neha et al. 2025). Ferrites are one of the most promising materials for photocatalytic degradation among the several types of photocatalyst. In the discipline of environmental science and technology, discovering permanent ways to minimize pollution has of greater significance than earlier. Employing ferrites for photocatalytic degradation is one exciting approach that has drawn interest from researchers and academics worldwide (Ahmad et al. 2016; Tong et al., 2012; Qin et al., 2021). Ferrites are a class of materials with unique properties that make them suitable for photocatalytic applications. Their high surface area, excellent stability, and low cost make them an attractive alternative to conventional catalysts. Unlike traditional methods of pollutant removal that often involve harsh chemicals and energy-intensive processes, ferrite-based photocatalysis is a clean

and sustainable approach. The application of ferrites is relatively new and unexplored. This opens up avenues for further research and discovery. Readers are intrigued by this topic because it offers a fresh perspective on solving environmental problems.

Future research endeavours should focus on addressing these challenges and exploring novel avenues, such as composite materials and advanced characterization techniques, to unlock the full potential of ferrites in environmental remediation. There are several ways to design nanoferrites, including physicochemical and environment friendly procedures. For nanoparticles generation, two general techniques namely top down and bottom-up methods have been reported. Using a top-down approach, macroscopic material is divided into nanoscale particles with the appropriate qualities (Ferreira et al., 2023). Chemical processes can be carried out using electrode positions, wet chemicals, spray pyrolysis, chemical reactions, direct precipitation, and combustion with microwave assistance. It has replaced the physiochemical technique, which focuses on making the environment more sustainable and less harmful. The method combines the generation of nanoferrites utilizing various plant and microbial components with beneficial biomedical uses (deOliveira et al., 2020). Different synthesis methods may change the catalysts structure, surface morphology and grain size, which may change the manner in which they operate as catalysts. Researchers may change the size, shape, and structure of the resultant products by varying reaction parameters including temperature, pressure and reaction time. As an instance, it is feasible to create nanoparticles with a more uniform size distribution by raising the reaction temperature or pressure. It is a vital instrument for both scientific study and industrial applications due to its capacity to regulate morphology and produce phase changes (Aisida et al., 2023). Co-precipitation is a common and very effective approach, which involves combining two or more precursor salts to create a precipitate. By changing reaction parameters like pH, temperature and molar ratio, this approach enables control over particle size distribution and composition.

In recent decades, the preparation and characterization of nanoparticles and nano-structured materials of various chemical compositions, structures and morphologies have become a topic area in inorganic materials research (Chakrabarty et al., 2015; Goldman, 2006; Laurent et al., 2008). Occupation of the tetrahedral sites entirely with a divalent metal ion produces a normal spinel structure, while the occupation of the octahedral site with the divalent metal ion yields an inverse spinel structure. If divalent metal ions are present on both (A) and (B) sub lattices, the structure is of mixed or disordered spinel

(Sickafus et al., 2004). X-ray diffraction, Mossbauer spectroscopy, Magnetization measurement, electron spin resonance (ESR), Neutron diffraction, Thermoelectric, and Nuclear magnetic resonance (NMR), Quantum mechanical method, and Rietveld refinement have been employed to determine the cation distribution in spinels. (Raghavender et al., 2008; Kurmude et al., 2014). In recent decades, the doped metal ions can substitute either A-site or B-site or both depending upon its valency and site type, which in turn affects the structural, electrical, and magnetic properties of the spinel ferrites (Ying et al., 2006). Thermodynamic considerations have shown that trivalent or tetravalent cations are usually positioned on octahedral sites, while divalent have no preference (Bordeneuve et al., 2010).

Magnetic materials in nano-size range have attracted interests of researchers due to their technological applications in catalysts, memory storage, sensors, magnetic-fluids, targeted drug delivery, bio-medical, hyperthermia, transformer core etc. (Goya et al., 2000; Hochepied et al., 2000). Further research in this area will undoubtedly contribute to our understanding of advanced materials and their applications in environmental remediation. While the potential of ferrites for photocatalytic degradation is promising, challenges such as scalability, long-term stability, and the need for further understanding of reaction mechanisms remain (Farhan et al., 2023). Ferrites of Nano-scale are utilized in microwave instruments as they have huge resistivity and also have low eddy current losses at high frequencies. Magnetic as well as dielectric characteristics of ferrites are based on their structure, composition and synthesis root. Ferrite nanoparticle is now the subject of considerable interest from both the industrial and academic sectors due to their contributions to the domains of sensing, medicines, and renewable energy sources. Photo catalysis is a versatile, user-friendly, and economical method for waste water treatment operations. Utilizing photocatalysis, one may lessen the harmful effects of contaminants and enhance the environment in which humans can live. Numerous contaminants that are easily discharged into the environment as a result of industrialization pose a hazard to aquatic environments and human life due to their toxicity.

## Literature review:

The aim of this research is to synthesize spinel Nano ferrite due to their wide range of application in modern world. Recently considerable research interests have attracted on structural, magnetic characterisation of these Nano ferrites. In addition, the

properties of these Nano ferrites can be tailored and controlled for practical purposes through substituting the appropriating divalent cations in their structure.

Abdo et al. (2024) have synthesized the $Ni_{0.5}Mn_{0.25}Co_{0.25}Ce_xFe_{2-x}O_4$ spinel nanoferrites by the citrate combustion method. The lattice strain and crystallite size of each Nickel Mangnase Cobalt Cerium Ferrites (NMCCF) nanoferrite were measured by evaluating the X-ray diffraction (XRD) results using Williamson-Hall plots. The crystallite size was between 40 and 78 nm. Fourier transform infrared spectroscopy (FTIR) analysis showed two strong frequency bands at 571 and 390 $cm^{-1}$, which are characteristic of spinel ferrites. Scanning electron microscopy SEM was used to investigate the particle size, composition, and distribution of the nanoferrites in the Nickel Mangnase Cobalt Cerium Ferrites (NMCCF) sample. The Nickel Mangnase Cobalt Cerium Ferrites (NMCCF5) nanoferrite exhibited a greater ability to remove methylene blue dye (97.38 %, within 60 min) compared to those materials.

Rajenimbalkar et al. (2024) synthesized the Nano scale spinel structured ferrites co-doped with tetravalent titanium ions ($Ti^{4+}$) and divalent zinc ions ($Zn^{2+}$) with general formula of $NiFe_{2-2x}Ti_xZn_xO_4$ ($x = 0.00 \leq x \leq 0.20$) in step of 0.05 by sol gel self-combustion method using citric acid as fuel to prepare the samples. The X-ray diffraction (XRD) analysis was performed which confirms the single-phase cubic spinel structure. The SEM was carried out which confirms sphere type grain morphology of the sample. The different surface parameters including surface area and pore volume was estimated using Brunauer-Emmett-Teller (BET) analysis. The low coercive nature with soft magnetism was observed with the co-doping as revealed by M-H plots.

Jasrotia et al. (2024) reported effect of synthesis methods, composites material and different doping strategies on efficiency of degradation of organic pollutants. It has been reported that due to small band gap and magnetic nature of magnesium ferrite, utilisation of broader spectrum of light is beneficial. Magnesium ferrite has excellent degradation within small duration of 1-2 hrs up to 90%. The different research work has reported exceptional photo catalytic characters due to its unique electrical band structure and surface properties.

Tejashwani et al. (2024) reported various industrial dyes which are harmful to environment. The nanomaterials are required to degrade the harmful dyes by selecting eco-friendly methods of nanomaterial's specially by using plant extracts. The characterisation of nanomaterial investigated the elemental doping for effective catalytic activity, morphological changes and various modification strategies.

Ramadan & Shafaay (2024) synthesized grapheme based Sm-doped Co-ferrite CoSmFe-G nanoparticles by using citrate auto combustion method. The XRD, FTIR, FE-SEM, VSM was carried out to analyse the physical properties of samples. The XRD results reveal single phase cubic spinel structure. The doping with grapheme and samarium change the magnetic properties of nanoparticles reduces the Ms values to 35.759 emu/g. The nanomaterial sample shows maximum lead adsorption with 99.8% of removal efficiency. These doped nanomaterial sample are used as efficient bio-adsorbent and antibacterial agent.

Khanvilkar et al. (2023) synthesized five Nano sized divalent and trivalent doped spinel ferrite by Co-precipitation method. The stoichiometry of the elemental composition of synthesized samples of nanomaterial was confirmed by EDS and ICPES The results of XRD confirmed the cubic structure with large lattice parameters in doped sample as compared to un-doped sample. The SEM and TEM studies the size and crystalline structure and histogram was found round about 18-52nm.

Cechinel et al. (2023) synthesized cobalt ferrite spinel by gel combustion which is used for degradation of water first time as a catalyst in Fenton process for Ramazol Red RR dye. XRD was carried out to determine the crystalline phase and crystallite size was 35 nm. SEM was carried out to determine the microstructure. The optimum dose of cobalt doped ferrite was determined. The synthesized nanoparticles show well define structure, large surface area and ferromagnetic properties which makes it effective catalyst for degradation of textiles dyes in contaminated water.

Dippong et al. (2022) reported the preparation method, microstructure, chemical composition, and particle size and shape which influence the spinel type ferrites. Adding other cations like $Co^{2+}$ can enhance ferrite characteristics, expanding their applications. The synthesis process, concentration, kind, composition, and placement of the cations all affect the structure and characteristics of ferrites. Furthermore, compared to bulk size particles, the nanoscaled ferrite particles exhibited superior optical, electrical, magnetic, and catalytic behaviour Additive substitutions, calcination processes, and synthesis techniques can all affect the ferrite structure and magnetic characteristics.

Dippong et al. (2021) reported the synthesis and characterization of nanosized ferrites has highly increased and a wide range of new applications. The paper reviews the synthesis methods and applications of $MFe_2O_4$ (M = Co, Cu, Mn, Ni, Zn) nanoparticles. $MFe_2O_4$ (M = Co, Cu, Mn, Ni, Zn) nanosized ferrites present good magnetic (high coercivity, high anisotropy, high Curie temperature, moderate saturation magnetization),

electrical (high electrical resistance, low eddy current losses), mechanical (significant mechanical hardness), and chemical (chemical stability, rich redox chemistry) properties that make them suitable for potential applications in the field of magnetic and dielectric materials, photoluminescence, catalysis, photocatalysis, water decontamination, pigments, corrosion protection, sensors, antimicrobial agents, and biomedicine.

Eisavi & Naseri (2021) synthesized the magnesium ferrite magnetic nanoparticles by solid state reaction and then calcination is carried out at high temperature. The XRD, TEM, EDS, FTIR, FESEM and VSM techniques identified the synthesized magnetic nanoparticles. The effects of various factors such as time, temperature, solvent and catalyst amount were investigated and optimum conditions was chosen to perform the reactions using 0.02 g of catalyst in water at 60 degree Celsius..

Desai et al. (2021) reported the synthesis of magnesium ferrite nanoparticles by auto combustion method. EDAX measurement was carried out to show elemental analysis. The XRD study shows the formation of spinel ferrite. The Debye - Scherrer equation was used to calculate the crystallite size of Nano ferrite using the intense peak of XRD. FTIR spectra validate the structure of nanoparticles and force constants was calculated for the interstitial sites of the spinel ferrites. The VSM analysis evaluates the superparamagenetic nature of Nano magnesium ferrite.

Han et al. (2020) have reported spinel-type $(Mg,Ni)(Fe,Al)_2O_4$ from saprolite laterite ore in large scale. The prepared $(Mg,Ni)(Fe,Al)_2O_4$ exhibited excellent photo-Fenton-like catalytic activity in decomposing different kinds of organic dyes and antibiotic tetracycline in the present of oxalic acid ($H_2C_2O_4$). The influential factors of RhB degradation efficiency were investigated, including the $(Mg,Ni)(Fe,Al)_2O_4$ dosage, $H_2C_2O_4$ concentration and the intensity of simulated sunlight. As the formation of highly photochemical $[Fe(C_2O_4)_3]^{3-}$ complex ions on the surface of the $(Mg,Ni)(Fe,Al)_2O_4$, the obtained $(Mg,Ni)(Fe,Al)_2O_4$ showed degradation efficiency ($\eta$) over 90.0 % for common organic dyes and antibiotic tetracycline within 180 min under the optimum conditions. The $\eta$ and TOC removal for RhB were still over 98.0 % and 46.0 % after five reuse cycles, respectively.

Bhuiyan et al. (2020) reported the synthesis of nano scaled iron oxide particles ($\alpha$-$Fe_2O_3$) were synthesized from hexahydrate ferric chloride ($FeCl_3.6H_2O$) with the addition of papaya leaf extract under atmospheric conditions. The synthesis of iron oxide nanoparticles was confirmed by systematic characterization using FTIR, XRD, FESEM, EDX and TGA studies. Increasing the dose of iron oxide nanoparticles enhanced the

decolorization of the dyes and a maximum 76.6% dye degradation was occurred at pH 2 after 6 hrs at a catalyst dose of 0.8 g/L. Unit removal capacity of the photocatalyst was found to be 340 mg/g at dye concentration of 70 ppm and at a catalyst dose of 0.4 g/L. The synthesized nanoparticles showed moderate antibacterial activity against *Klebsiella* spp., *E.Coli, Pseudomonas* spp., *S.aureus* bacterial strains.

Dutta et al. 2019 reported the cobalt ferrite has gained huge consideration in the field of semiconductor photocatalysis for waste water treatment. Cobalt ferrite and its derivatives own tunable magnetic properties which results in higher absorption capability in comparison with other photocatalyst semiconductors. For the enhancement of photocatalytic action of cobalt ferrite, the role of cobalt ferrite with type I, type II, direct Z-scheme, solid state Z-scheme heterojunctions, Schottky and p-n heterojunctions based on different heterostructures were also discussed.

Arshad et al. (2019) synthesized the nickel and cobalt doped manganese Nano ferrite by using co-precipitation method and noticed the structural, magnetic and dielectrical properties. XRD of the sample was carried out which reveals spinel structure having crystallite size 27-35 nm. M-H loops of Nano ferrite was studied which indicate that by increasing the Co-Ni contents, saturation magnetisation increased up to X=0.15 and thereafter decreases.

Bindu & Nagaraja (2019) synthesized nickel doped iron oxide nanoparticles by microwave assisted method. The samples were annealed at 450 degree Celsius and 600 degree Celsius. To study the structural, thermal, morphological and compositional properties of the samples XRD, TGA, SEM and EDX were carried out. Hematite phase was reported at both 450 degree Celsius and 600 degree Celsius in case of un-doped sample. After nickel doping, two transitions temperature in TGA and intermediate phase were noticed. VSM studies reveal ferromagnetic behaviour in doped samples at both temperatures except un-doped sample at 600 degree Celsius shows antiferromagnetic behaviour.

Rohit et al. (2018) have reported the photocatalytic and dielectric studies of Ni doped Mg-Zn nanoferrites. The spinel nanoferrites have been synthesized by co-precipitation technique. An enhanced photocatalytic study has been reported for the samples under study with increase in Ni content and irradiation time. For 50 min exposure of x = 0.500 sample, a maximum degradation efficiency of 36.94% has been reported.

Ehi-Eromosele et al. (2018) reported the synthesis and antimicrobial activity of magnesium ferrite ($MgFe_2O_4$) and cobalt doped magnesium ferrite ($Co_{0.8}Mg_{0.2}Fe_2O_4$) spinel nanoparticles. These nanoparticles are synthesized by low temperature combustion method and characterised by XRD, SEM, EDAX. The XRD analysis confirmed the cubic spinel structure and SEM analysis exhibit the formation of multigrain fine crystallite. The sample does not contain any impurities and composition was closer to normal value. The ($Co_{0.8}Mg_{0.2}Fe_2O_4$) show high antibacterial effects against E. coli and S. aureus 2500 microgram/mL and 1250 microgram /mL respectively.

Rohit et al. (2017) reported $Ni^{2+}$ doped $Mg_{0.5}Zn_{0.5-x}Fe_2O_4$ (x=0,0.125, 0.250, 0.375, 0.500) ferrite samples prepared by co-precipitation methods and are characterised by XRD, FT-IR, FE-SEM for various physical properties. A transition has been reported from superparamagnetic behaviour to soft paramagnetic nature with the addition of $Ni^{2+}$. Ferrite nanoparticles have shown an increase in coercivity with lower saturation magnetisation with reduction in the crystallite size.

Akhtar et al. (2017) reported that whether super exchange interactions can lead to an improvement in the structural and magnetic characteristics of spinel nanoferrites by substituting metal ions. There are also effects on these qualities.

Rohit et al. (2016) has reported an improvement in magnetic characterstics in $Co^{2+}$ substituted Mg single bond Zn nano ferrites synthesized by co-precipitation method. Physical properties have been studied for $Mg_{0.5}Zn_{0.5-xCox}Fe_2O_4$ ( x = 0, 0.125, 0.250, 0.375, 0.500) nanoferrites using XRD, FTIR, FESEM, EDS,VSM etc. single phase cubical spinel has been reported. Saturation magnetisation has been found to be enhanced.

Ponraj et al. (2017) have reported the different effluents from textile industries which are dumped into the water bodies have been a major concern of the modern world. The uncontrolled discharge of the synthetic textile dyes in water bodies especially have led to serious environmental problems and health hazards. Among the different existing approaches to treat water, photocatalysis is an attractive approach as it uses the inexhaustible and clean solar energy. Considering its ability to absorb in the visible light of solar spectrum, its multiferroic property and its crystal structure, researchers feel $BiFeO_3$ can provide a breakthrough in the treatment of water.

Kulkarni et al. (2013) have reported the nanostructured Mn–Ni–Zn ferrites with composition $Mn_{0.1}Ni_{0.6}Zn_{0.3}Al_xFe_{(2-x)}O_4$ (where x = 0.05, 0.1, 0.15, 0.2) have been prepared by sol–gel method. The structural data obtained by X-ray diffraction (XRD) of

all Mn–Ni–Zn nanoferrites confirmed the spinel structure. The XRD data was used to calculate the lattice parameter and grain size. The morphology of nanoferrites was studied using scanning electron microscopy. The elemental composition (atomic percentage) was determined with the help of energy dispersive X-ray analyser. Vibrating sample magnetometry was used to study the magnetic properties of nanoferrites. High saturation magnetization of value 38.7 emu/g, coercivity 7 Oe and highest initial permeability 83.7 are measured for the sample consisting x = 0.05 Al concentration.

Sridhar et al. (2012) have reported the synthesis of mixed copper substituted nickel Nano ferrites by citrate gel technique having chemical formula $Ni_{1-x}Cu_xFe_2O_4$ (where 0.0.2, 0.4, 0.6, 0.8, 0.9 and 1.0). The XRD and SEM were carried out to study the crystal structure and morphology. EDS were studied to determine the elemental composition. The XRD diffraction pattern confirmed the crystallite size in the range 36-58nm having single phase cubic spinel structure. The increase in Cu substitution in Ni ferrites decreases the lattice parameters. The densification of the material exhibits increase in X-ray density with increase of Cu substitution in Ni ferrites.

Burauh et al. (2012) have reported the environmental pollution and industrialization on a global scale have drawn attention to the vital need for developing new hygienically friendly purification technologies. Application of nanotechnology that results in improved water treatment options might include removal of the finest contaminants from water (< 300 nm) and "smart materials" or "reactive surface coatings" with engineered specificity to a certain pollutant that destroy, transform or immobilize toxic compounds. Nanomaterials have been gaining increasing interest in the area of environmental remediation mainly due to their enhanced surface and also other specific changes in their physical, chemical and biological properties that develop due to size effects.

Zhuang et al. (2012) have reported the temperature sensitive ferrofluid has been prepared by dispersing oleic acid modified $Mn_{1-x}Zn_xFe_2O_4$ nanoparticles into hydrocarbon based carriers. $Mn_{1-x}Zn_xFe_2O_4$ nanoparticles with good crystalline quality and magnetic properties were synthesized by a novel modified hydrothermal process with purification of precursor. Crystalline and magnetic properties of $Mn_{1-x}Zn_xFe_2O_4$ particles with different $x$ were discussed. $Mn_{1-x}Zn_xFe_2O_4$ particles show a high saturation magnetization up to 54.6 emu/g and low Curie points ($T_C$, most are below 100 °C). Sharp magnetic-temperature gradients are observed at $T_C$ for all samples with different Zn content (13.0 emu/g/K in the case of $Mn_{0.5}Zn_{0.5}Fe_2O_4$).

Hu et al. (2008) have reported the magnetic $MFe_2O_4$ (M=Co, Ni, Zn) nanocrystals with a diameter about 30 nm and a nearly spherical shape were synthesized via a simple hydrothermal approach. X-ray diffraction, scanning electron microscopy, and transmission electron microscopy have been used to investigate the as-prepared magnetic $MFe_2O_4$ (M=Co, Ni, Zn) nanocrystals. Magnetic properties of the as-prepared samples have been detected by a vibrating sample magnetometer at room temperature and the results show that the as-prepared magnetic $MFe_2O_4$ nanocrystals are a type characteristic of superparamagnetic materials.

Toledo-Antonio (2002) have reported the non-stoichiometric zinc ferrites, which were used as catalysts for the oxidative dehydrogentation of 1-butene, were synthesized by using co-precipitation and hydrothermal methods. Their atom local order was analyzed with Mossbauer spectroscopy and the refinement of the crystalline structures; their macroscopic magnetization was measured by the vibrating sample method.

## Research Gap Identification:

There is limited research on the use of transition metal doped spinel ferrite for environmental and biomedical applications such as heavy metal ion adsorption from industrial effluents, antimicrobial, antibacterial properties etc. Most studies have focused on the synthesis and basic characterization of transition metal doped spinel nanoferrites with limited research on their long-term stability and performance in real-world applications. There is a need for research on the doped spinel nanoferrites for its wide range of applications. Some areas where significant research gaps exist in the field of spinel ferrites:

- Current synthesis methods are not easily scaleable for industrial application.
- High costs of precursor materials
- limited research on green synthesis
- Insufficient understanding of magnetic properties
- Lack of detailed studies on distribution of metal ions in crystal lattice
- Limited study of relationship between nanoparticle size and magnetic properties
- Limited study on thermal stability and corrosion resistance
- Limited study on biocompatibility in drug delivery
- Limited study on catalytic activity of spinel ferrite.
- Poor understanding of adsorption mechanism for removing heavy metals

- Lack of accurate computational models to predict properties based on composition and synthesis.
- Limited study of recyclability.

## Objectives:

The objectives of this research are:

- To synthesize transition metal doped spinel nanoferrites by wet chemical synthesis and their structural, morphological and magnetic study.
- Optimization of sintering temperature for further study of spinel nanoferrites.
- Doping of divalent metal ion at different concentrations.
- To evaluate the potential of metal doped spinel nanoferrites for memory storage, environmental and biomedical applications.

## Proposed Methodology:

The following steps will be taken during the research work as below:

Wet chemical synthesis of spinel ferrite nanoparticles. Co-precipitation synthesis technique will be used for the synthesis of $MgFe_2O_4$ ferrite powder. The starting materials, magnesium chloride, iron (III) chloride and NaOH will be procured from Thermo Fisher Scientific India (98% purity) and are used as received. In 80 ml of distilled water, 3M solution (1M magnesium chloride + 2M iron (III) chloride) of starting materials will be prepared (say stock 1). In 200 ml of distilled water, 4M NaOH solution will be prepared (say stock 2). The stock 1 will be poured into the boiling solution of NaOH under stirring. The value of pH will noticed throughout the co-precipitation. The reaction will be put to force at 80°C - 85°C temperature for an hour under energetic stirring. The obtained precipitates will be left to settle at room temperature. The obtained precipitates will be washed several times with distilled water followed by overnight drying in a hot air oven at 100°C. The dried sample will be crushed to powder with the help of mortar and pestle. Some of the dried powdered sample will be divided into four parts and subjected to different sintering temperatures for optimization. After sintering, the samples will be characterized using X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), EDS (Energy-Dispersive X-Ray Spectroscopy) and Fourier transform infrared spectra (FTIR), VSM (Vibrating Sample Magnetometer). The doping of primary Precursor of nanoferrite will be carried out with divalent transition metal in varying concentration ranges and characterisation of doped Precursors will be carried out using X-ray diffraction (XRD),

field emission scanning electron microscopy (FE-SEM), EDS (Energy-Dispersive X-Ray Spectroscopy) and Fourier transform infrared spectra (FTIR), VSM (Vibrating Sample Magnetometer). The applications of nanoferrites will be carried out in the field of memory storage, antimicrobial activity and dyes degradation.

## Thesis Outline:

***Chapter 1 (Introduction):*** This chapter will include the introduction of spinel nano ferrites and their structural and magnetic properties, effect of dopants on structural and magnetic properties of spinel nanoferrites.

***Chapter 2 (Literature review):*** This chapter will include the various researches of different authors. This chapter will also include the research gap identified.

***Chapter 3 (Materials and Methods):*** This chapter will include the details of the experiments used and instrumental details. This chapter also includes the techniques and steps used in the research.

***Chapter 4 (Results and Discussions):*** This chapter deals with the results/outcomes of the identification and desired application of the synthesized nanoferrites.

***Chapter 5 (Summary and Conclusions):*** This chapter will comprise summary of entire study according to objectives along with conclusions. This chapter also include the future scope of the research.

***Chapter 6 (References):*** This chapter includes the references of books, reports, research papers of the authors associating in the ongoing research.

## References:


Abdo, M. A., S. F., Mansour & N. S., Al-Bassami (2024) Enhancing the magnetization, dielectric parameters and elastic parameters while simultaneously minimizing coercively and dielectric loss in nickel-manganese-cobalt ferrite nanoparticles through $Ce^{3+}$ doping assistance. *Ceramics international*. 50 (21), 43433-43441. Available from: https://doi.org/10.1016/j.ceramint.2024.08.194

Ahmad, R., Ahmad, Z., Khan, A. U., Mastoi, N. R., Aslam, M. & Kim, J. (2016) Photocatalytic systems as an advanced environmental remediation: Recent developments, limitations and new avenues for applications. *Journal of Environmental chemical Engineering* 4 (4), 4143–4164. Available from: https://doi.org/10.1016/j.jece.2016.09.009

Aisida, S. O., Chibueze, T. C., Alnasir, M. H., Oyewande, O. E., Raji, A. T., Ekuma, C. E., Ahmad, I., Zhao, T-K., Maaza, M. & Ezema, F. I. (2023) Microstructural and

magneto-optical properties of $Co_{1-x}Ni_xFe_2O_4$ nanocomposites for hyperthermia applications. *Solid State Sciences.* 136, 107107. Available from: https://doi.org/10.1016/j.solidstatesciences.2022.107107

Arshad, M., Asghar, M., Junaid, A., Warsi, M. F., Rasheed, M. N., Hashim, M., Al-Maghrabi, M. A. & Khan, M. A. (2019) Structural and magnetic properties variation of manganese ferrites via Co-Ni substitution. *Journal of magnetism and magnetic materials*. 474, 98-103. Available from: https://doi.org/10.1016/j.jmmm.2018.10.141

Baruah, S., Pal, S. K. & Dutta, J. (2012) Nanostructured zinc oxide for water treatment, *Nanoscience & Nanotechnology-Asia.* 2 (2) 90–102. Available from: http://dx.doi.org/10.2174/2210681211202020090

Bindu, K. & Nagaraja, H. S. (2019) Temperature - dependant phase transformation of $Ni_xFe_{y-x}O_z$ nano ferrite: their dielectric and magnetic properties. *Applied Physics A*. 125,448. Available From: https://doi.org/10.1007/s00339-019-2737-z

Bhuiyan, M. S. H., Miah, M. Y., Paul, S. C., Aka, T. D., Saha, O., Rahaman, M. M., Sharif, M. J. I., Habiba, O. & Ashaduzzaman, M. (2020) Green synthesis of iron oxide nanoparticle using Carica papaya leaf extract: application for photocatalytic degradation of remazol yellow RR dye and antibacterial activity. *Heliyon.* 6 (8), e04603. Available from: https://doi.org/10.1016/j.heliyon.2020.e04603

Bordeneuve, H., Tenailleau, C., Guillement-Fritsch, S., Smith, R., Suard, E. & Rousset, A. (2010) Structural variations and cation distributions in $Mn_{3-x}Co_xO_4$ ($0 \leq x \leq 3$) dense ceramics using neutron diffraction data. *Solid State Sciences*. 12 (3) 379-386. Available From: https://doi.org/10.1016/j.solidstatesciences.2009.11.018

Cechinel, M. A. P., Nicolini, J. L., Tapia, P. M., Miranda, E. A. C., Eller, S., de Oliveira, T. F., Pereira, F. R., Montedo, O.R.K., Wermuth, T. B &; Arcaro, S. (2023) Cobalt ferrite spinel as a new efficient magnetic heterogeneous Fenton-like catalyst for wastewater treatment. *Sustainability*. 15 (20), 15183. Available From: https://doi.org/10.3390/su152015183

Chakrabarty, S., Pal, M. & Dutta, A. (2015) Structural, optical and electrical properties of chemically derived nickel substituted zinc ferrite nanocrystals. *Materials Chemistry and Physics.* 153, 221-228. Available from: https://doi.org/10.1016/j.matchemphys.2015.01.006

de Oliveira, P. F. M., Torresi, R. M., Emmerling, F. & Camargo, P. H. C. (2020) Challenges and opportunities in the bottom-up mechanochemical synthesis of noble

metal nanoparticles. *Journal of Materials Chemistry* A. 8 (32) 16114–16141. Available from: https://doi.org/10.1039/D0TA05183G

Desai, Harshal B., Kumar, A., & Tanna, Ashish R., (2021) Structural and magnetic property of $MgFe_2O_4$ ferrite nanoparticles synthesis through auto combustion technique. *European Chemical Bulletin, European Chemica* 10 (3), 186-190. Available From: https://doi.org/10.17628/ecb.2021.10.186-190

Dippong, T., Toloman, D., Dan, M., Levei, E. A., Mare, B, Cedar, O. (2022) Structutal, morphological and photocatalytic properties of Ni-Mn ferrites: Influence of the Ni: Mn ratio. *J. Alloys Compd.* 913, 165129. Available from: https://doi.org/10.1016/j.jallcom.2022.165129

Dippong, T., Levei, E. A., & Cadar, O. (2021) Recent Advances in Synthesis and Applications of $MFe_2O_4$ (M = Co, Cu, Mn, Ni, Zn) Nanoparticles. *Nanomaterials.* 11 (6), 1560. Available from: https://doi.org/10.3390/nano11061560

Dutta, V., Singh, P., Shandilya, P., Sharma, S., Raizada, P., Saini, A. K., Gupta, V. K., Hosseini-Bandegharaei, A., Agarwal, S. & Rahmani-Sani, A. (2019) Review on advances in photocatalytic water disinfection utilizing graphene and graphene derivatives-based nanocomposites. *Journal of Environmental Chemical Engineering.* 7 (3) 103132. Available from: https://doi.org/10.1016/j.jscs.2019.07.003

Ehi- Eromosele, C. O., Olugbuyirozz, J. A. O., Taiwo, O. S., Bamgboye, O. A. & Ango, C. E. (2018) Synthesis and evaluation of the antimicrobial potentials of cobalt doped and magnesium ferrite spinel nanoparticles. *Bulletin of the Chemical Society of Ethiopa.* 32 (3), 451-458. Available from: http://dx.doi.org/10.4314/bcse.v32i3.4

Eisavi, R. & Naseri, K. (2021) Preparation, characterisation and application of $MgFe_2O_4$/ Cu nanocomposite as a new magnetic catalyst for one pot regioselective synthesis of beta-thiol-1-4-disubstituted-1,2,3-triazoles. *Royal Society of Chemistry Advances.* 11 (22), 13061-13076. Available From: http://dx.doi.org/10.1039/D1RA01588E

Farhan, A., Arshad, J., Rashid, E.U., Ahmad, H., Nawaz, S., Munawar, J., Zdarta, J., Jesionowski, T. & Bilal, M., (2023) Metal ferrites-based nanocomposites and nanohybrids for photocatalytic water treatment and electrocatalytic water splitting. *Chemosphere.* 310, 136835. Available from: https://doi.org/10.1016/j.chemosphere.2022.136835

Ferreira, M. E. C., Bernardino, E. G., de Barros, M. A. S. D., Bergamasco, R. & Yamaguchi, N. U. (2023) An overview of nanostructured manganese ferrite as a promising visible-light-driven photocatalyst for wastewater remediation. *Journal of*

*Water Process Engineering.* 54, 104049. Available from: https://doi.org/10.1016/j.jwpe.2023.104049

Fujiwara, T. (1985) Barium ferrite media for perpendicular recording. *IEEE Transactions of magnetics.* 21 (5), 1480-1485. Available from: https://doi.org/10.1109/TMAG.1985.1064091

Goldman, A., *Modern Ferrite Technology*, Springer-Verlay, PA, 2006 Pittsburgh. ISBN : 978-0-387-28151-3.

Goya, G. F., Rechenberg, H. R., Chen, M.& Yelon, W. B. (2000) Magnetic irreversibility in ultrafine $ZnFe_2O_4$ particles. *Journal of Applied physics.* 87 (11), 8005-8007. Available from: https://doi.org/10.1063/1.373487

Han, X., Liu, S., Huo, X., Cheng, F., Zhang, M. & Guo, M. (2020) Facile and large-scale fabrication of $(Mg,Ni)(Fe,Al)_2O_4$ heterogeneous photo-Fenton-like catalyst from saprolite laterite ore for effective removal of organic contaminants. *Journal of Hazardous Materials.* 392, 122295. Available from: https://doi.org/10.1016/j.jhazmat.2020.122295

Hu, C., Gao, Z. & Yang, X. (2008) One –pot low temperature synthesis of $MFe_2O_4$ (M=Co,Ni,Zn) superparamagnetic nanocrystals. *Journal of Magnetism and Magnetic materials.* 320 (8), L70-L71. Available from: https://doi.org/10.1016/j.jmmm.2007.12.006

Hochepied, J. F., Pileni, M. P. (2000) Magnetic properties of mixed Cobalt-Zinc ferrite nanoparticles. *Journal of Applied Physics.* 87 (5) 2472-2478. Available from: https://doi.org/10.1063/1.372205

Hylton, T., Parker, M., Ullah, M., Coffey, K. R., Umphress, R. & Howard, J.K. (1994) Ba-ferrite thin film media for high density longitudinal recording. *Journal of Applied Physics.* 75 (10), 5960-5965. Available From: https://doi.org/10.1063/1.356987

Jasrotia, R., Jaswal, N., Prakash, J., Kit, C. C., SINGH, J. & Kandwal, A. (2024) Photocatalytic application of magnesium spinel ferrite in wate water remediation: A review. *Journal of Magnesium and Alloys.* 12 (2), 490-505. Available from: https://doi.org/10.1016/j.jma.2024.02.006

Khanvilkar, M. B., Nikumbh, A. K., Pawar, R. A., Karale, N. J., Nagwade, P. A., Nighot, D. V., Gugale, G. S., Sangale, M. D., Misal, S. B., & Panchgalle, S. P. (2023) Effect of divalent/trivalent doping on structural, electrical and magnetic properties of spinel nanoferrite nanoparticles. *Engineered Science.* 22,850. Available From: https://dx.doi.org/10.30919/es8d850

Khot, V. M., Salunkhe, A. B., Phadatare, M. R., Thorat, N. D. & Pawar, S. H. (2013) Low temperature synthesis of $Mn_xMg_{1-x}Fe_2O_4$(x=0-1) nanoparticles: cation distribution, structural and magnetic properties. *Journal of Physics D: Applied Physics*. 46 (5), 055303. Available from: https://dx.doi.org/10.1088/0022-3727/46/5/055303

Kulkarni, S. R., Londhe, P. U. & Chaure, N. B. (2013) Electrical and magnetic properties of $Al^{3+}$ substituted Mn-Ni-Zn nanoferrite. *Journal of materials science: materials in electronics*. 24, 4186-4191 Available from: https://doi.org/10.1007/s10854-013-1381-1

Kumar, L., Kumar, P. & Kar, M. (2013) Infilunce of Mn substitution on crystal structure and magnetocrystalline anisotropy of nanocrystalline $Co_{1-X}Mn_XFe_{2-2X}Mn_{2X}O_4$. *Applied Nanoscience*. 3, 75-82. Available from: http://dx.doi.org/10.1007/s13204-012-0071-2

Kurmude, D. V., Barkule, R. S., Raut, A. V., Shengule, D. R. & Jadhav, K. M. (2014) X-ray diffraction and cation distribution studies in zinc-substituted nickel ferrite nanoparticles. *Journal of Superconductivity and Novel Magnetism*. 27, 547-553. Available From: https://doi.org/10.1007/s10948-013-2305-2

Laurent, S., Forge, D., Port, M., Roch, A., Robic, C., Elst, L. V., Muller, R. N. (2008) Magnetic iron oxide nanoparticles: synthesis, stabilization, vectorization, physicochemical characterizations, and biological applications. *Chemical Reviews*. 108 (6), 2064- 2110. Available from: https://doi.org/10.1021/cr068445e

Ponraj, C., Vinitha G., & Daniel, J. (2017) A review on the visible light active $BiFeO_3$ nanostructures as suitable photocatalyst in the degradation of different textile dyes. *Environmental Nanotechnology Monitoring Management*. 7, 110–120. Available from: https://doi.org/10.1016/j.enmm.2017.02.001

Qin, H., He, Y., Xu, P., Huang, D., Wang, Z., Wang, H., Wang, Z., Tian, Q. & Wang, C. (2021) Spinel ferrites ($MFe_2O_4$): Synthesis, improvement and catalytic application in environment and energy field. *Advances in Colloid and Interface Science*. 294, 102486. Available from: https://doi.org/10.1016/j.cis.2021.102486

Raghavender, A. T., Kulkarni, R. G., Jadhav, K. (2008) Magnetic Properties of Nanocrystalline Al Doped Nickel Ferrite Synthesized by the Sol-Gel Method. *Chinese Journal of Physics*. 46 (3) 366-375. Available From: https://www.airitilibrary.com/Article/Detail?DocID=05779073-200806-46-3-366-375-a [Accessed 3rd January 2025]

Ramadan, R., & Shafaay, A. S. (2024) Graphene based Sm-doped Co-ferrite for environmental applications. *Journal of Materials Science: Materials in Electronics.* 35, 1331. Available From: https://doi.org/10.1007/s10854-024-12980-z

Rajenimbalkar, R. S., Deshmukh, V. J., Patankar, K. K. & Somvanshi, S.B. (2024) Effect of multivalent ion doping on magnetic, electrical, and dielectric properties of nickel ferrite nanoparticles. *Scientific. Report.* 14, 29547. Available from: https://doi.org/10.1038/s41598-024-81222-3

Rezlescu, N., Rezlescu, E., Popa, P. D., Doroftei, C. & Ignat, M. (2014) Scandium substituted nickel-cobalt ferrite nanoparticles for catalyst applications. *Applied catalysis B: Environmental.* 158-159, 70-75. Available from: https://doi.org/10.1016/j.apcatb.2014.03.052

Sharma, R., Thakur, P., Kumar, M., Sharma, P. & Sharma, V. (2018) Nanomaterials for high frequency device and photocatalytic applications: Mg-Zn-Ni ferrites. *Journal of alloys and Compounds.* 746, 532-539. Available from: https://doi.org/10.1016/j.jallcom.2018.02.287

Sharma, R., Thakur, P., Sharma, P. & Sharma, V. (2017) Ferrimagnetic $Ni^{2+}$ doped Mg-Zn spinel ferrite nanoparticles for high density information storage. *Journal of Alloys and Compounds.* 704, 7-17. Available from: https://doi.org/10.1016/j.jallcom.2017.02.021

Sharma, R., Thakur, P., Kumar, M., Thakur, N., Negi, N. S., Sharma, P. & Sharma, V. (2016) Improvement in magnetic behaviour of cobalt doped magnesium zinc nano-ferrites via-co-precipitation route. *Journal of Alloys and Compounds*. 684, 569-581. Available from: https://doi.org/10.1016/j.jallcom.2016.05.200

Sickafus, K. E., Wills, J. M. & Grimes, N. W. (2004) Structure of Spinel. *Journal of American Ceramic Society.* 82 (12) 3279-3292. Available from: https://doi.org/10.1111/j.1151-2916.1999.tb02241.x

Sridhar, R., Ravinder, D., Kumar, V. K. (2012) Synthesis and characterisation of copper substituted nickel nano-ferrites by citrate gel technique. *Advances in Materials Physics and Chemistry.* 2 (3) 192-199. Available from: http://dx.doi.org/10.4236/ampc.2012.23029

Sun, C., Lee, J. S., & Zhang, M. (2008) Magnetic nanoparticles in MRI and drug delivery. *Advanced drug delivery reviews.* 60 (11) 1252-1265. Available from: https://doi.org/10.1016/j.addr.2008.03.018

Tejashwani, D. M., Harini, H. V., Nagaswarupa, H. P., Naik, R., Harlapur, S. & Basavaraju, N. (2024) Nanoferrite in photocatalytic wastewater treatments: Advancements, characterisation and environmental implications. *Results in chemistry* 7, 101247. Available from: https://doi.org/10.1016/j.rechem.2023.101247

Thakur, N., Sharma, I., Thakur, P., (2025) Spinel Ferrite Materials: Fundamentals,Progress and applications. Woodhead Publishing Series in Electronics and Optical Materials. 1-30. Available from: https://doi.org/10.1016/B978-0-443-21742-5.00001-2

Tong, H., Ouyang, S., Bi, Y., Umezawa, N., Oshikiri, M., Ye, J. (2012) Nano-photocatalytic materials: possibilities and challenges. *Advanced Materials*. 24 (2), 229–251. Available from: https://doi.org/10.1002/adma.201102752

Toledo-Antonio, J. A., Nava, N., Martinez, M., Bokhimi, X. (2002) Correlation between the magnetism of non- stoichiometric Zinc ferrites and their catalytic activity for oxidative dehydrogenation of 1-butene. *Applied Catalysis* A: General 234 (1-2), 137-144. Available from: https://doi.org/10.1016/S0926-860X(02)00212-0

Wu, H., Liu, G., Wang, X., Zhang, J., Chen, Y., Shi, J., Yang, H., Hu, H. & Yang. S. (2011) Solvothermal synthesis of cobalt ferrite nanoparticles loaded on multiwalled carbon nanotubes for magnetic resonance imaging and drug delivery. *Acta Biomaterialia*.7 (9), 3496-3504. Available from: https://doi.org/10.1016/j.actbio.2011.05.031

Ying, W., Yu, K. X., Xiong, Y. & Hui, W. (2006) EPR investigation of the site symmetry of Fe3+ ions in the spinel crystals. *Physica B: Condensed Matter*. 381 (1-2), 260-264. Available From: https://doi.org/10.1016/j.physb.2006.01.495

Zhuang, L., Zhang, W., Zhao, Y., Li, D., Wu, W., Shen, H. (2012) Temperature sensitive ferrofluid composed of $Mn_{1-}$ $xZn_xFe_2O_4$ nanoparticles prepared by a modified hydrothermal process. *Powder Technoogyl.* 217, 46–49. Available from: https://doi.org/10.1016/j.powtec.2011.10.007

Supervisor 29/01/2025.

Prof. (Dr.) Yogesh Kumar Walia,

Department of Chemistry, School of Basic and Applied Sciences,

Career Point University Hamirpur, H.P., India

Co-Supervisor

Prashant Thakur
29-01-2025

Dr. Prashant Thakur, Assistant Professor,

Department of Physics, School of Basic and Applied Sciences,

Career Point University Hamirpur, H.P., India

Research Scholar 29/01/25

Anil Kumar (UID: H240598)

Department of Chemistry, CPUH (H.P.), India

# CERTIFICATE
## (SYNOPSIS APPROVAL CERTIFICATE)

This is to certify that the Synopsis titled, **"Transition Metal Doped Nanoferrites: Study of Structural and Magnetic properties",** submitted by **Mr. Anil Kumar** to the Career Point University, Hamirpur (H.P.), India in partial fulfillment of the requirements for the degree of **DOCTOR OF PHILOSOPHY** in the **Department of Chemistry, School of Basic and Applied Sciences** has been approved by the Research Advisory Committee (RAC) after an Oral Examination of the student on dated 07/01/2025

29/01/25

Dr.Yogesh Kumar Walia, Professor, Department of Chemistry, Career Point University, Hamirpur (H.P.) – 176041, India

**(Supervisor)**

**Research Advisory Committee**

Prashant Thakur 29-01-2025

Dr. Prashant Thakur,
Assistant Professor, Deptt. of Physics,
CPU Hamirpur, H.P., India
**(Co-Supervisor)**

Dr. Kuldeep Kumar,
Assoc. Professor Department of Chemistry, CPU Hamirpur,(H.P.)
**(RAC Member)**

Dr. Gulshan Kumar,
Assistant Professor, Division Botany,
CPU, Hamirpur (H.P.)
**(RAC Member)**

Dr. Asha Kumari, CPU, Hamirpur (H.P.)
**(Head, Department of Chemistry)**

Dr. Kuldeep Kumar, CPU, Hamirpur (H.P.)
**(Dean R & D)**